Resonance and Relaxation [Organic spectroscopy - Jag Mohan]

The phenomenon of energy absorption by an oscillating medium, when there is a correspondance between the frequency of the incoming signal and that of the medium, is known as resonance.

The nuclei in an external applied field H_0, are precessing in two orientations, the energy difference between them is given by the following relation:

$$E = \frac{\mu H_0}{I}$$

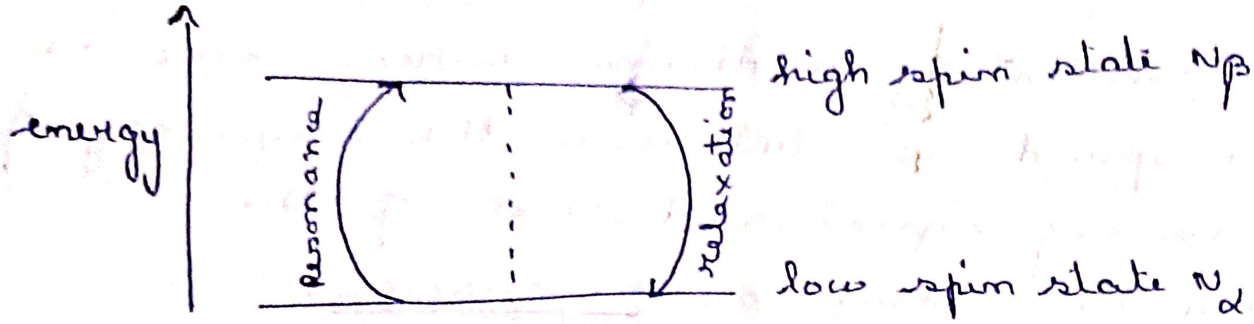
I - nuclear spin

μ - magnetic moment

For $I = 1/2$

$E = 2\mu H_0$

When energy equal to $2\mu H_0$ is supplied to a proton system, a hydrogen nucleus undergoes transition from one spin state to another. The energy required for transition can be supplied by electromagnetic radiation in the radio-frequency range. If the magnetic field r_0 of the radiation is oscillating in a plane at right angle to the applied field (H_0) and the frequency of radiation is the same as the larmor frequency of precession (ν_L) of the nuclei, then the transfer of energy from the radiation to the nuclei will take place leading to the phenomenon of resonance as shown below.



N_α, N_β - population of spin states.

(Fig) Resonance and Relaxation.

Relaxation phenomenon :

Relaxation phenomenon involves transition of an excited proton which returns to the ground state by loss of its energy but without the emission of radiation.

Consider a system of protons distributed between the two energy level states (α and β) aligned with or against the applied field, at the thermal equilibrium.

The relative population of the higher and lower energy states can be calculated at the thermal equilibrium from the Boltzmann distribution law, as per the equation

$$\frac{N_\alpha}{N_\beta} = e^{\Delta E / KT} \simeq 1 + \frac{\Delta E}{KT}.$$

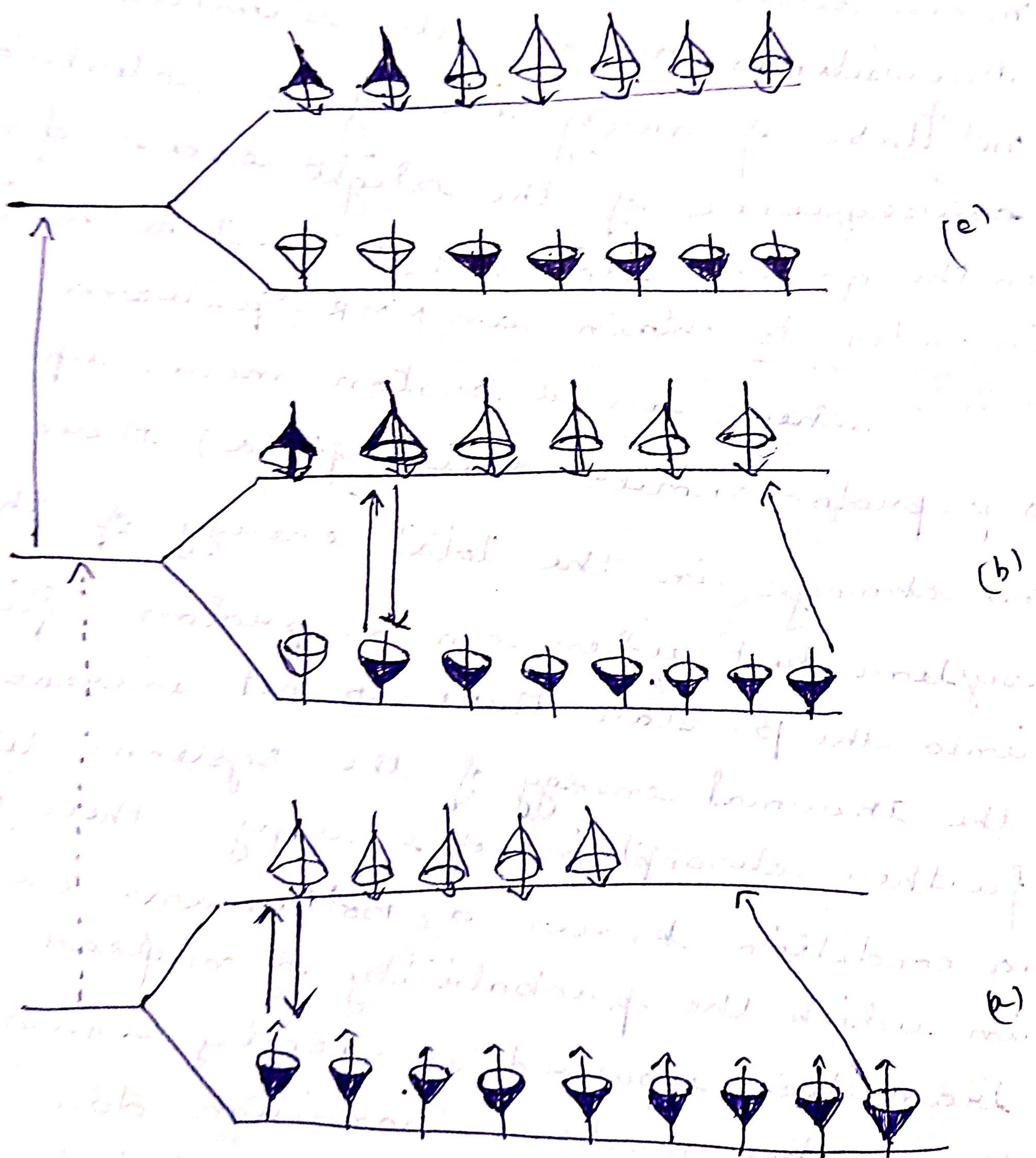
$$= 1 + \frac{2\mu H_0}{KT}.$$

where N_α and N_β are the number of nuclei in the α (lower energy) and β (higher energy) states respectively. ②

when a radio frequency signal is applied to the system, transitions of spinning nuclei will occur, upward and downward transitions are equally stimulated but the net uptake of energy is only a statistical consequence of the slight excess of nuclei in the ground state which must be maintained in order to obtain an NMR spectrum.

when an α proton moves up and a β-proton moves down fig (a) there is no change in the total energy of the system but when an α-proton flips into the β-state there is net increase in the thermal energy of the system. With further absorption of energy, there exists a condition known as Boltzmann condition in which the probability of nuclear transition upward is exactly equal to the ~~number~~ nuclear transition downward and the population of the nuclei in the

the two states become equal. If this were absolutely true, no NMR signal would be observed because of the cancellation of equal number of nuclei in opposite spin states. The system is said to be saturated and no further net absorption can take place until relaxation occurs.

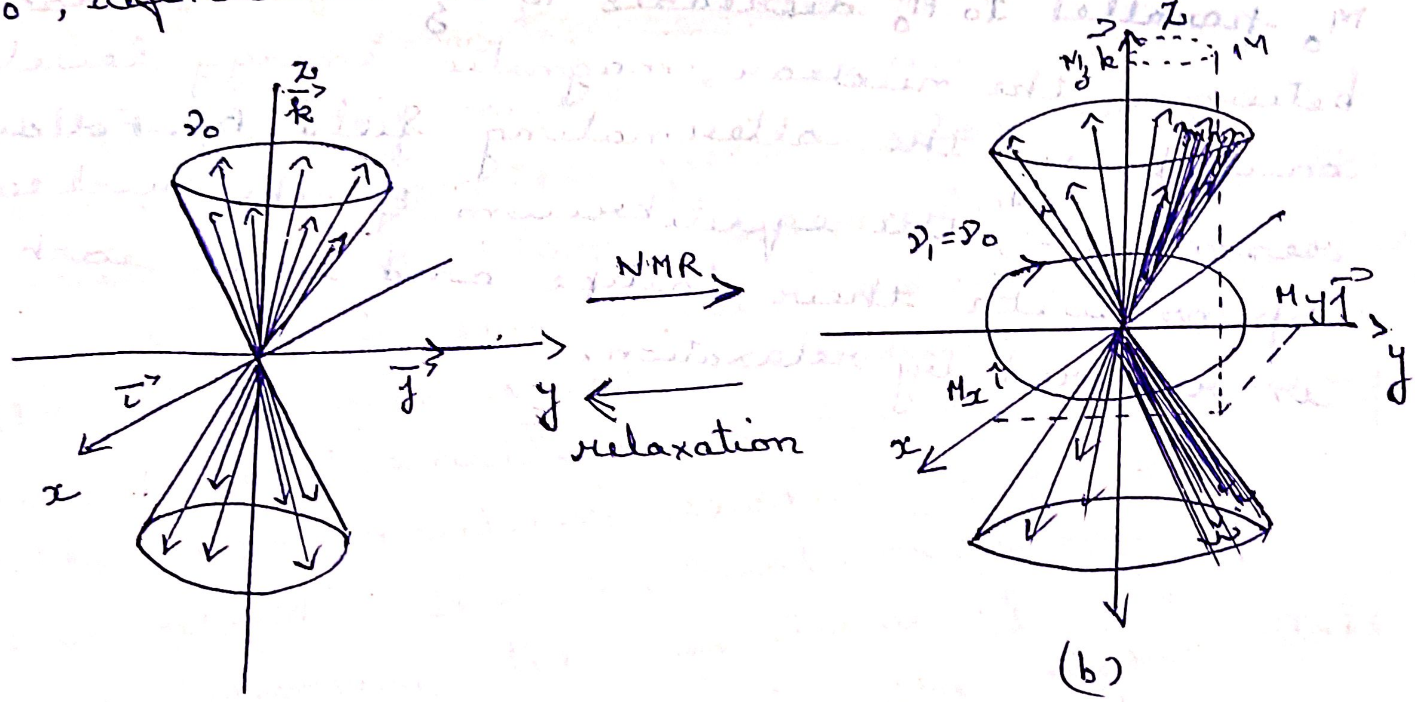


Fig(a) distribution of nuclei b/w lower and higher energy states.

magnetic vectors

The Boltzmann factor, $\frac{2\mu_0 H_0}{KT}$, only slightly favours the lower spin-state and is important to study the influence of magnetic fields on an assembly of a large number of identical nuclei than on one spinning nucleus.

For an assembly of identical nuclei with $I = 1/2$, two orientations with respect to H_0 are possible for each of the nucleus. Due to the favouring of the lower state with spin alignment more nearly parallel to H_0, more nuclei process about the direction of H_0, defined as the +z direction Fig (a)



(a) vectors of magnetization in equilibrium

(b) vector of magnetization at resonance. $\nu_1 = \nu_0$

The application of an RF field B_1 with frequency ν_1 disturbs the equilibrium and

and consequently the magnetic moment vectors μ are forced to process in phase fig (b).

The resultant magnetisation vector M is no longer parallel to H_0 fig (b) and is now composed of three components along the axes x, y and z. These components are related to M by the equation using the unit vectors i, j k along x, y and z as illustrated in the fig b

$$M = M_x \vec{i} + M_y \vec{j} + M_z \vec{k}.$$

$M_z \vec{k}$ is the longitudinal magnetization along the z-axis, $M_x \vec{i}$ and $M_y \vec{j}$ make up the transverse magnetization in the xy plane.

At resonance, the equilibrium magnetization M_0 parallel to H_0 decreases to M_z due to transitions between the nuclear magnetic energy levels caused by the alternating field B_1. Following resonance, the equilibrium of the nuclear spins with their lattice and with each other is restored by relaxation.